Demixing in a single-peak distributed polydisperse mixture of hard spheres

José A. Cuesta*

Grupo Interdisciplinar de Sistemas Complicados (GISC), Departamento de Matemáticas, Escuela Politécnica Superior, Universidad Carlos III de Madrid, c/ Butarque, 15, 28911 – Leganés, Madrid, Spain

An analytic derivation of the spinodal of a polydisperse mixture is presented. It holds for fluids whose excess free energy can be accurately described by a function of a few moments of the size distribution. It is shown that one such mixture of hard spheres in the Percus-Yevick approximation never demixes, despite its size distribution. In the Boublík-Mansoori-Carnahan-Starling-Leland approximation, though, it demixes for a sufficiently wide log-normal size distribution. The importance of this result is twofold: first, this distribution is unimodal, and yet it phase separates; and second, log-normal size distributions appear in many experimental contexts. The same phenomenon is shown to occur for the fluid of parallel hard cubes.

PACS: 61.20.Gy, 64.75.+g, 82.70.Dd

Our knowledge of the phase behavior of mixtures has increased a lot in the last decade. Generally speaking, above a certain concentration binary mixtures phase separate due to the socalled depletion effect [1]. This mechanism has an entropic origin: mixtures phase separate when this produces a sufficient gain in free volume to increase the entropy of the system. More intuitively, depletion is an effective attraction arising from the unbalance pressure resulting when two solute particles are so close together that no solvent particle fits in between them. Either way we look upon it, in real colloids this mechanism is supplemented by energetic attractions or repulsions that enhance or inhibit the transition. This is the reason why most theoretical research has focused in additive hard particle mixtures, in order to ascertain to which extent depletion is the basic mechanism of demixing

Binary hard spheres (HS), the simplest hard-particle mixture, has proven very controversial in settling the question. More than thirty years ago Lebowitz and Rowlinson [2] showed that according to the Percus-Yevick (PY) solution of the Ornstein-Zernike equation binary HS never demix; a few years later Vrij [3] extended this result to p-component HS mixtures in the same approximation. However, the PY approximation has a well known thermodynamic inconsistency, as it yields two different equations of state, none of which being very accurate at large densities. It is also well known that a linear interpolation of both produces a rather accurate equation of state; in the case of mixtures, the latter is known as the BMCSL equation of state [4,5]. In spite of its higher accuracy, the authors showed that it predicts the stability of any binary mixture.

The BMCSL equation of state is heuristic in its construction, so this led Biben and Hansen [6] to consider the more accurate Rogers-Young closure approximation. In this way they found signs of a spinodal instability for diameter ratios of the HS smaller than 0.2. Several authors [7,8] subsequently confirmed that other approximate schemes yield the same instability, although for diameter ratios strongly dependent on the approximation. It was hence believed that phase separation does occur in sufficiently asymmetric binary mixtures of HS, an idea further supported by the demixing found in binary mixtures of parallel hard cubes (PHC) both in computer simulations on a lattice [9] and from fundamental measure theory [10] in continuum space.

Presently a different scheme is being accepted to describe demixing of very asymmetric binary mixtures of hard particles [11]: phase separation occurs between a small-particle rich fluid and a large-particle rich crystal [12–17], and this coupling with the translational degrees of freedom strongly enhances demixing. It may even cause, for very large asymmetry, the appearance of an isostructural solid-solid transition [15–17] as that found for narrow and deep attractive potentials—the reason being that depletion induces one such potential between the large particles [15–18].

But colloids are hardly mono or bidisperse. By their very nature, colloidal particles are usually different from each other, and the preparation process of a colloidal suspension gives rise to a size distribution of particles in the colloid. Hence colloids are best modeled as polydisperse systems. Polydispersity has received increasing attention in the past years [19–26] because it causes strong qualitative effects on the phase behavior of the monodisperse counterpart. Termination of the freezing transition of a HS fluid [21,22], regularization of adhesive potentials [25,17], or appearance of a vapor-liquid transition in adhesive HS [26] are but a few examples.

Phase equilibrium in polydisperse systems is more complicated than in monodisperse systems: equilibrium equations between coexisting phases become functional equations when polydispersity is present [19,20]. Much of the effort has indeed concentrated in taking advantage of extra symmetries (as the dependence of the excess free energy on the moments of the distribution [23,24]), or in mapping the polydisperse system into a simpler one (e.g. a binary mixture [22]), with the purpose of reducing

equilibrium to a few algebraic equations. Specifically, by means of a moment-based formalism [23,24] Warren [27] has shown that while a binary fluid of HS in the BMCSL approximation never demixes, it does if enough polydispersity is introduced and the diameter ratio of the two "main" species is sufficiently small. This unexpected result proves that the effect of polydispersity can be more subtle and nontrivial than one can tell a priori.
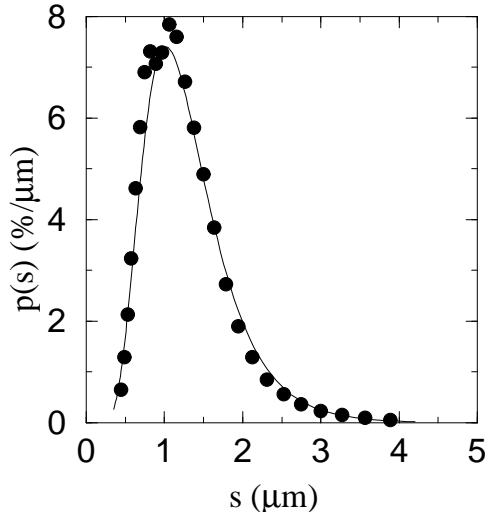

FIG. 1. Distribution, $p(s)$ (in percentage per μm), of diameters, s (in μm), for a suspension of *mullite* ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), a ceramic powder used in structural ceramic applications. Bullets are the experimental data; the line is a fit of a log-normal distribution of mean $\overline{x} = 1.57$ μm and variance $w = 0.43\overline{x}$. (Experimental data courtesy of R. Moreno, Instituto de Cerámica y Vidrio, CSIC, Madrid, Spain.)

In this letter I will push this result much further. Though polydisperse, Warren's system has two clearly differentiated species. I will show that for demixing to occur this is not necessary if the size distribution decays sufficiently slowly. Again using a moment-based formalism (equivalent to Warren's but based on different grounds) to obtain a spinodal of an arbitrary mixture (with several species, polydisperse, or both), I will prove that BCSML polydisperse HS with a *log-normal* size distribution (i.e. the logarithm of the diameters follows a normal distribution) phase separate provided the variance of the distribution is above a threshold. This result is surprising because one such distribution is unimodal. It is thus clear that the long-size tail plays a crucial role in inducing demixing, but although slowly decaying, this tail decays faster than any power-law. In addition, it is important to stress that, contrary to what one might believe, log-normal distributions are very common in many polydisperse systems: ultrafine metal particles, paint and rubber pigments, photographic emulsions, dust particles, aerosols, cloud droplets, or suspensions of ceramic powders (see [28] and references therein; see also Fig. 1), etc.

Therefore this effect should be experimentally accessible, provided any of these systems can be prepared with sufficiently large size dispersion.

In what follows I will briefly describe the formalism to obtain the spinodal in the case that the excess free energy of a mixture depends on a few moments of the size distribution. Then I will apply this formalism to polydisperse HS and PHC in scaled particle approximation (equivalent to PY in the case of HS), and I will finally prove the above mentioned result.

Suppose we have a multicomponent hard particle mixture, whose free energy per unit volume is $f \equiv \beta F/V = f^{\text{id}} + f^{\text{ex}}$, with $f^{\text{id}} = \sum_i \rho_i[\log \mathcal{V}_i\rho_i - 1]$, $\mathcal{V}_i$ the thermal volume of species i, β the reciprocal temperature (in units of the Boltzmann constant), and ρ_i the number density of species i. Let us further assume that $f^{\text{ex}} = \phi(\xi)$, ξ denoting the set of moments $\{\xi_0, \xi_1, \ldots, \xi_p\}$, where $\xi_k = \sum_i \sigma_i^k \rho_i$ (σ_i is the diameter of species i). Stability of the mixture requires f to be a convex function in all of its variables. As in any hard particle system f depends on temperature through an additive term (the free energy of the ideal gas) and hence it is always convex with respect to this variable. The study of stability is thus restricted to the set of densities of the species involved. If we define the matrix

$$\mathsf{M} \equiv \frac{\partial^2 f}{\partial \rho_i \partial \rho_j} = \frac{1}{\rho_i}\delta_{ij} + \frac{\partial^2 \phi}{\partial \rho_i \partial \rho_j}, \qquad (1)$$

then stability requires it to be positive definite. As it is so for low densities (ideal mixtures are always stable) the spinodal is usually described as the set of points in the densities space where $|\mathsf{M}| = 0$ ($|\cdot|$ denotes the determinant) [2,29]. This condition is equivalent to M having a zero eigenvalue, i.e. $\mathsf{M} \cdot \mathbf{u} = 0$ for some vector $\mathbf{u} \neq 0$. Let us define for convenience a new vector $\mathbf{e}$ as $u_i = \rho_i e_i$; then $\mathsf{M} \cdot \mathbf{u} = 0$ means

$$e_i = -\sum_j \frac{\partial^2 \phi}{\partial \rho_i \partial \rho_j}\rho_j e_j. \qquad (2)$$

For a polydisperse mixture, if $\rho(s) = \rho p(s)$, where ρ is the total number density of particles and $p(s)$ is the size probability distribution (in terms of a dimensionless diameter s, for instance), $f^{\text{id}} = \int ds\, \rho(s)[\log \mathcal{V}(s)\rho(s) - 1]$ [19], $\xi_k = \int ds\, s^k\rho(s)$, but f^{ex} is still assumed to be of the form $f^{\text{ex}} = \phi(\xi)$. The stability condition is now the positive definiteness of the integral operator whose kernel is defined by

$$\mathcal{M}(s,t) \equiv \frac{\delta^2 f}{\delta\rho(s)\delta\rho(t)} = \frac{1}{\rho(s)}\delta(s-t) + \frac{\delta^2 \phi}{\delta\rho(s)\delta\rho(t)}. \qquad (3)$$

While the determinant condition has no direct equivalent for an integral operator, the zero-eigenvalue one is a straightforward extension of (2):

$$e(s) = -\int dt\, \frac{\delta^2 \phi}{\delta\rho(s)\delta\rho(t)}\rho(t)e(t). \qquad (4)$$

2

But we can simplify this equation by using

$$\frac{\delta^2 \phi}{\delta \rho(s) \delta \rho(t)} = \sum_{k,l=0}^{p} \frac{\partial^2 \phi}{\partial \xi_k \partial \xi_l} s^k t^l, \qquad (5)$$

which transforms Eq. (4) into

$$e(s) = - \sum_{k,l=0}^{p} \Phi_{kl} s^k \alpha_l, \qquad \Phi_{kl} \equiv \frac{\partial^2 \phi}{\partial \xi_k \partial \xi_l}, \qquad (6)$$

where $\alpha_l = \int ds\, s^l \rho(s) e(s)$. Substitution of Eq. (6) into the latter definition yields [31]

$$\alpha_n = - \sum_{k,l=0}^{p} \xi_{n+k} \Phi_{kl} \alpha_l. \qquad (7)$$

For this equation to have nonzero solutions for α we must have $|\mathsf{Q}| = 0$, with

$$\mathsf{Q}_{mn} \equiv \delta_{mn} + \sum_{k=0}^{p} \xi_{m+k} \Phi_{kn}, \quad m,n = 0, \ldots, p. \qquad (8)$$

For convenience we introduce the variables $y_k \equiv \xi_k/(1-\xi_3)$ and define two new matrices, Y and Ω, by $\mathsf{Y}_{mn} \equiv y_{m+n}$ and $\Omega \equiv (1-\xi_3)\Phi_{mn}$. Then the condition reads $\mathcal{D} \equiv |\mathbb{I} + \mathsf{Y} \cdot \Omega| = 0$, with $\mathbb{I}$ the identity matrix.

Many scaled-particle theories can be written [10,30,32]

$$\phi = -\xi_0 \ln(1-\xi_3) + A\frac{\xi_1 \xi_2}{1-\xi_3} + B\frac{\xi_2^3}{(1-\xi_3)^2}. \qquad (9)$$

(Notice that if ϕ and ξ_k are all multiplied by the same constant the product $\mathsf{Y} \cdot \Omega$ remains invariant, so we will assume these variables defined up to a constant.) For this particular choice of ϕ we will have

$$\Omega = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & A & Ay_2 \\ 0 & A & 6By_2 & Ay_1 + 6By_2^2 \\ 1 & Ay_2 & Ay_1 + 6By_2^2 & y_0 + 2Ay_1y_2 + 6By_3^3 \end{pmatrix}. \qquad (10)$$

It is then straightforward to check that

$$\mathcal{D} = \frac{[1 + (1-A)\xi_3]^2 + (6B - A^2)\xi_2 \xi_4}{(1-\xi_3)^4}, \qquad (11)$$

where we have replaced the y's in terms of the ξ's; ξ_3 is the volume fraction of the fluid. We are now ready to discuss specific cases.

Percus-Yevick HS correspond to choosing $A = 3$, $B = 3/2$ (definitions of ϕ and ξ_k carry an extra $\pi/6$ factor); then $\mathcal{D} = (1+2\xi_3)^2/(1-\xi_3)^4$, the result obtained by Lebowitz and Rowlinson [2] for the binary mixture and later generalised by Vrij [3] for a multicomponent mixture. The validity of this result has now been extended for a polydisperse mixture [31].

Scaled-particle free energy for PHC is given by [10,30] $A = 3$, $B = 1$. Then

$$\mathcal{D} = [(1 + 2\xi_3)^2 - 3\xi_2\xi_4]/(1-\xi_3)^4. \qquad (12)$$

By a suitable choice of ξ_2 and ξ_4 we can make $\mathcal{D} = 0$. If we consider a binary mixture we recover the result of Ref. [10]. By defining $m_k \equiv \xi_k/\xi_3 = \int ds\, s^k p(s)$, the mixture of PHC in this approximation will be stable provided $K(\xi_3) > m_2 m_4$, where $K(\xi_3) \equiv (1 + 2\xi_3)^2/(3\xi_3^2)$. The function $K(x)$ diverges at $x = 0$ and it monotonically decreases to 3 as ξ_3 approaches 1. Then $m_2 m_4 > 3$ is the condition to find demixing, and the larger the product $m_2 m_4$ the smaller the value of ξ_3 at which it appears.

Schulz distribution is a common choice in studying polydispersity [19]. If the mean is set to 1, it can be written as

$$p(s) = w^{-2}\Gamma(w^{-2})(w^{-2}s)^{w^{-2}-1}e^{-w^{-2}s}, \qquad (13)$$

with $0 < w < 1$ the variance. Its moments are $\xi_n = \rho \prod_{k=0}^{n-1}(1 + kw^2)$ for $n \geq 1$, so $m_2 m_4 = (1 + 3w^2)/(1 + 2w^2) < 4/3$. Therefore there is no demixing for such a distribution. It is easy to check that there is no demixing either for a uniform distribution in any interval of diameters. However if we consider a log-normal distribution with mean 1 and variance $0 < w < \infty$,

$$p(s) = \frac{1 + w^2}{\sqrt{2\pi \ln(1 + w^2)}} \exp\left\{ -\frac{\ln^2[(1 + w^2)^{3/2}s]}{2\ln(1 + w^2)} \right\}, \qquad (14)$$

whose moments are given by $\xi_n = \rho(1 + w^2)^{n(n-1)/2}$, then $m_2 m_4 = 1 + w^2$, which, by increasing w, can be made arbitrarily large. There is thus demixing for a log-normal distribution provided $w > \sqrt{2}$.

The latter result rises the question whether the same occurs for BMCSL HS. In this case the free energy is given by [19]

$$\phi = \left(\frac{\xi_2^3}{\xi_3^2} - \xi_0 \right) \ln(1 - \xi_3) + \frac{3\xi_1 \xi_2}{1 - \xi_3} + \frac{\xi_2^3}{\xi_3(1 - \xi_3)^2}, \qquad (15)$$

where, as in PY, ϕ and ξ_k are defined with an extra $\pi/6$ factor. The difference with respect to the PY one is

$$\Delta\phi = \xi_2^3 \left\{ \frac{1}{\xi_3^2} \ln(1 - \xi_3) + \frac{1 - 3\xi_3/2}{\xi_3(1 - \xi_3)^2} \right\}, \qquad (16)$$

where $\Delta\phi \equiv \phi_{\mathrm{BMCSL}} - \phi_{\mathrm{PY}}$. The corresponding matrix $\Omega_{\mathrm{BMCSL}} = \Omega_{\mathrm{PY}} + \Delta\Omega$, where $\Delta\Omega$ is obtained from the second derivatives of $\Delta\phi$ (its only nonzero elements $\Delta\Omega_{jk}$ are those with $j, k = 2, 3$).

The resulting expression for $\mathcal{D}$ with the moments replaced by those of a log-normal distribution is a complicated formula relating the volume fraction, ξ_3, and the variance, w; nevertheless, the spinodal can be numerically determined (Fig. 2). It can be seen that the

threshold variance for demixing is $w \approx 1.6$. The inset shows the size distribution for a variance for which the spinodal occurs at liquid densities, in order to illustrate the long tail at large particle sizes. Comparing with Fig. 1 and with the figures of Ref. [28] we can see that standard experimental samples are still far from reaching the spinodal.
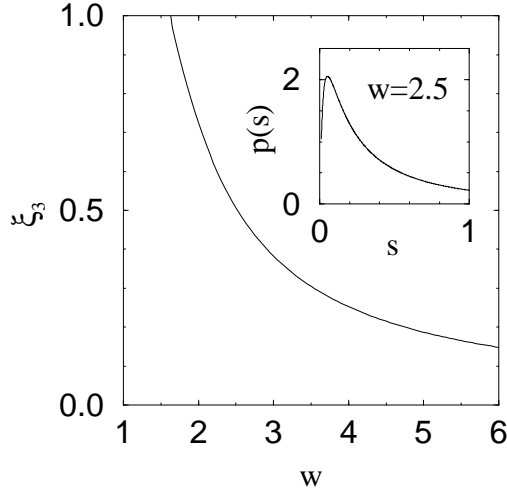

FIG. 2. Volume fraction, ξ_3, as a function of the variance of the log-normal size distribution, w, at which a spinodal instability appears. Inset: size distribution for the particular value $w = 2.5$.

In summary, I have introduced a simple formalism to compute the spinodal of fluids whose excess free energy can be described as a function of a few moments of the size distribution of a mixture. By means of this formalism I have proven that a polydisperse mixture of PY HS never demixes despite its size distribution. I have also shown that a polydisperse mixture of PHC may demix only if the size distribution is long-tailed at large sizes, as for instance a log-normal distribution. More importantly, polydisperse BMCSL HS, also log-normally distributed, do demix for a sufficiently large variance. Remarkably, log-normal distributions have a single characteristic size, so the driving mechanism of the transition in these systems is not as clearcut as in the case of binary mixtures. Finally, sizes in many polydisperse systems are log-normally distributed. Present experimentally available systems, though, are far from the spinodal as predicted by this work. I hope that this result encourages experimental work to achieve this limit and verify the conclusions reported here.

∗   E-mail: cuesta@math.uc3m.es

[1] S. Asakura and F. Oosawa, J. Chem. Phys. **22**, 1255 (1954).
[2] J. L. Lebowitz and J. S. Rowlinson, J. Chem. Phys. **41**, 133 (1964).
[3] A. Vrij, J. Chem. Phys. **69**, 1742 (1978).
[4] T. Boublik, J. Chem. Phys. **53**, 471 (1970).
[5] G. A. Mansoori, N. F. Carnahan, K. E. Starling, and T. W. Leland, Jr., J. Chem. Phys. **77**, 3714 (1982).
[6] T. Biben and J.-P. Hansen, Phys. Rev. Lett. **66**, 2215 (1991).
[7] H. N. W. Lekkerkerker and A. Stroobants, Physica A **195**, 387 (1993).
[8] Y. Rosenfeld, Phys. Rev. Lett. **72**, 3831 (1994).
[9] M. Dijkstra and D. Frenkel, Phys. Rev. Lett. **72**, 298 (1994); M. Dijkstra, D. Frenkel and J.-P. Hansen, J. Chem. Phys. **101**, 3179 (1994).
[10] J. A. Cuesta, Phys. Rev. Lett. **76**, 3742 (1996).
[11] This general scheme may change if the particles have internal degrees of freedom (e.g. rotations); see M. Dijkstra and R. van Roij, Phys. Rev. E **56**, 5594 (1997).
[12] A. Imhof and J. K. G. Dhont, Phys. Rev. Lett. **75**, 1662 (1995).
[13] W. C. K. Poon and P. B. Warren, Europhys. Lett. **28**, 513 (1994).
[14] C. Caccamo and G. Pellicane, Physica A **235**, 149 (1997).
[15] N. García-Almarza and E. Enciso in *Proceedings of the VIII Spanish Meeting on Statistical Physics FISES '97*, p. 159, J. A. Cuesta and A. Sánchez, eds. (Editorial del CIEMAT, Madrid, 1998).
[16] M. Dijkstra, R. van Roij, and R. Evans, submitted to Phys. Rev. Lett. (1998).
[17] Y. Martínez–Ratón and J. A. Cuesta, preprint cond-mat/9804225 (1998).
[18] T. Biben, P. Bladon, and D. Frenkel, J. Phys.: Condens. Matter **8**, 10799 (1996).
[19] J. J. Salacuse and G. Stell, J. Chem. Phys. **77**, 3714 (1982).
[20] J. A. Gualteri, J. M. Kincaid, and G. Morrison, J. Chem. Phys. **77**, 521 (1982).
[21] P. G. Bolhuis and D. A. Kofke, Phys. Rev. E **54**, 634 (1996).
[22] P. Bartlett, J. Chem. Phys. **107**, 188 (1997).
[23] P. Sollich and M. E. Cates, Phys. Rev. Lett. **80**, 1365 (1998).
[24] P. B. Warren, Phys. Rev. Lett. **80**, 1369 (1998).
[25] G. Stell, J. Stat. Phys. **63**, 1203 (1991).
[26] R. P. Sear, preprint cond-mat/9805201 (1998).
[27] P. B. Warren, preprint (1998).
[28] C. G. Granqvist and R. A. Buhrman, Appl. Phys. Lett. **27**, 693 (1975); J. Appl. Phys. **47**, 2200 (1976).
[29] H. B. Callen, *Thermodynamics* (Wiley, N. Y., 1960).
[30] J. A. Cuesta and Y. Martínez-Ratón, Phys. Rev. Lett. **78**, 3681 (1997); J. Chem. Phys. **107**, 6379 (1997).
[31] This result can also be obtained, by the same procedure, from Eq. (2), and so is valid for both multicomponent and polydisperse mixtures (or a combination of both).
[32] Y. Rosenfeld, Phys. Rev. E **50**, R3318 (1994).